THE USE OF METHANOL AS A MOTOR VEHICLE FUEL

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I. Blends of Methanol and Gasoline as Motor Vehicle Fuels

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The use of methanol has been suggested as a means of extending the nation's supply of liquid fuels. The transportation sector of the economy is one of the largest users of liquid fuels today, and several investigations have been made of the possibility of blending portions of methanol with gasoline to extend the supply of that fuel. The data reported from several of these investigations together with the particular experiences encountered have been gathered together in a report prepared for the City of Seattle by Mathematical Sciences Northwest, Inc. The sections of this report are summarized here together with pertinent references.

Fuel Consumption (1, 2, 3, 4, 5, 6, 7, 9, 14, 17, 18)

The energy content of methanol is less than that of gasoline (8640 Btu/lb vs 19,080 Btu/lb) so that higher fuel consumption would be theoretically predicted for blends of methanol and gasoline than for straight gasoline. However, these blends will burn more satisfactorily at sub-stoichiometric fuel to air ratios than will gasoline, and this fact together with their better anti-knock qualities and cooler, more efficient engine operation may offset this theoretical prediction. Depending upon the automobile engine tested, fuel economy has been shown to be improved slightly or slightly decreased by the addition of methanol to form blended fuels. Since the blend contains less Btu per gallon, there is a slight but significant increase in efficiency of operation on a mile per Btu basis. This increase is generally reported, and may be of importance economically depending upon the comparative prices of gasoline and methanol on a dollars per million Btu basis.

Power or Acceleration (6,8,9,10,14)

The high latent heat of vaporization of the methanol (474 Btu/lb vs 141 Btu/lb for octane) cools the air charge of an engine and increases its density. This causes an increase in volumetric efficiency and available power from an engine. However, the methanol also lowers the combustion temperature in the cylinder, resulting in lower combustion efficiency. It has been shown that the addition of practical amounts of methanol to gasoline should not appreciably affect the power output of an unmodified automobile engine.

<u>Vapor Pressure</u> (9, 11, 13, 14, 18)

Because of the disruption of hydrogen bonding in methanol when it is mixed with a hydrocarbon, the vapor pressure of a mixture of methanol and gasoline deviates greatly from ideal behavior as predicted by Raoult's Law, exhibiting a much higher vapor pressure than would be expected. This excess vapor pressure can lead to vapor lock problems, difficulties with hot starts, stalling, hesitation, and poor

acceleration. The evaluation of these problems is highly subjective, however. This question will be discussed after three more factors affecting driveability are mentioned.

Solubility (2,6,7,8,9,11,15,17)

Another factor affecting the driveability of an automobile fueled with a methanol-gasoline blend is the degree of solubility of the methanol in the base gasoline. Methanol is least soluble in paraffins and napthenes, and more soluble in aromatics and unsaturates. Therefore, the amount of aromatics in the base gasoline greatly affects the degree to which the methanol will blend. At lower temperatures the solubility of methanol in gasoline is decreased. Operation in subfreezing environments will be a problem, and suitable solubilizers such as higher alcohols will have to be added to the fuel.

Separation (1, 3, 4,6,7,9,11,14,15,17,19,20,21,22,23,24)

The presence of very small amounts of water can cause methanolgasoline mixtures to separate into gasoline and water-alcohol phases.
These separate phases are vastly different in their combustion properties. Some of the aromatics from the base gasoline will also separate
with the alcohol-water leaving the gasoline phase very low in octane
number. The separation becomes more pronounced at low temperatures so
that the primary effect will be very difficult, if not impossible, cold
starting and stalling in cold weather. As with solubility the properties of the blend are dependent upon the aromatic content of the base
gasoline. As the methanol fraction increases in a blend so does the
water tolerance. The presence of higher alcohols in the blend increases
its water tolerance. The problem of phase separation of methanolgasoline blends can be a serious one. The solution may lie in the addition of higher alcohols to the blend.

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Octane Number (1,3,6,7,8,9,11,14,15,17,18,20,21,28)

Pure methanol has a very high blending octane value (BOV). This number reflects the fact that the blending of methanol with gasoline is a very effective method of increasing the octane number of the fuel. The effect is less pronounced in newer automobiles. The elimination of knocking has been demonstrated as the result of this effect. Higher compression ratios may be utilized and the attendant increases in fuel economy realized. The effective increase in octane number depends upon the octane number of the base gasoline used in the blend. Methanol is more effective in raising the octane number of an originally lower octane number fuel. One of the most interesting effects of this octane number boost is the possibility of replacing tetra-ethyl-lead as an anti-knock compound in gasoline with a low percentage of methanol in a blend, helping to minimize lead pollution. The substitution of methanol for TEL in gasolines as an anti-knock agent will prevent the accidental poisoning of catalytic mufflers by lead.

<u>Subjective Road Tests</u> (1,3,6,7,8,14,15,17,19,20,24,25,29)

The overall effect upon driveability resulting from the properties of methanol gasoline blends that were discussed in the preceding

sections can only be assessed through subjective fleet tests in which some qualitative judgments of overall driveability are given by drivers of automobiles in actual field tests. These qualitative judgments can only be subjective, and as such are open to the effects of bias; however, care is taken (blinds) to minimize these effects.

One specific area that has been investigated is the effect upon cold starting. Difficult cold starting has been predicted. Cold start problems are decreased by the addition of higher alcohols to the fuel. Subjective judgments of the effects of methanol blends used as fuels on driveability seem as mixed as the driver's assessments of automobiles themselves. Perhaps it can be safely stated that the substitution of a 7 percent blend of methanol would exhibit enough beneficial effects to overshadow most detrimental effects. However, this number depends strongly upon the specific automobile considered and the severity of the cold weather to be encountered in service.

Corrosion and Compatibility (1,2,6,7,9,11,13,14,15,17,24,26,27,29)

The automotive fuel system has been developed for the use of petroleum distillates and the substitution of blends of methanol for fuels opens the possibility of corrosion of fuel system parts. The gasket materials and elastomer seals used in the automotive fuel system must also be examined for compatibility with methanol fuel blends. Several test programs have been carried out in this area, and also observations have been made of the effects of corrosion during most of the fleet tests that have been performed.

Methanol and methanol blends have been seen to attack the terne plating on automobile fuel tanks. Deterioration of copper, aluminum and magnesium has also been reported.

There appear to be serious corrosion and compatibility problems associated with the use of methanol blends in some automobile fuel systems. There are similar problems when pure methanol is used as a fuel; however, the greater problem is experienced with blends primarily because of the water separation problem. The corrosion and compatibility problems listed above are not universally observed, however. It appears as if the severity of the corrosion and compatibility problem depends strongly upon the particular vehicle and fuel system being considered. Certain specific problems such as those with methacrylate fuel filters and Viton float valve seats can be identified; however, it is very difficult to generalize further.

Modifications and Reliability (1,3,6,8,11,14,15,21,24)

One of the beneficial aspects of the use of methanol as a blend with gasoline should be the fact that engine modifications are not necessary. The degree of adherence to this dictum depends upon the percentage of methanol considered, the age of the automobile, and the tolerance of the driver. Problems of driveability that point to the necessity of equipment modifications increase with methanol concentration. Older, richer cars are more tolerant of the leaning effect of methanol blends. Equipment reliability has not been sufficiently examined in the time scale of the experiments that have been carried out, except for the corrosion problems mentioned in the previous section. Further testing needs to be done before sufficient data are

available to make valid conclusions concerning equipment reliability.

Emissions

One of the most beneficial effects of the use of methanol blends as automotive fuels is the reduction in the emission of air pollutants afforded. This reduction, together with the octane number boost, has been the motivating factor in most of the investigations of the use of methanol blends as automotive fuels.

Carbon Monoxide Emissions (2,3,5,6,8,14,21,23,24,25,30)

The emission of carbon monoxide (CO) from an automotive engine is decreased when methanol blends are substituted for straight gasoline as a fuel without vehicle modifications because of the leaning effect of the blend and the more complete burning of the fuel that is afforded. The blending of methanol with gasoline has been shown to decrease the emissions of carbon monoxide in the vehicle exhaust if the vehicle is unmodified and allowed to take advantage of the leaner operation possible with methanol blends. Indeed, the fact that the engine need not be modified for the use of methanol blends is one of the motivating factors for the use of such blends and should be considered a ground-rule for vehicle testing in which the use of blends is investigated. Comparison of the data with the Federal Standards points out the fact that the use of methanol blends will not obviate the incorporation of catalytic converters in order to meet the 1977 standard for CO emissions.

Hydrocarbon Emissions (2,5,6,9,14,21,24,30,31)

The effect of the use of methanol blends as fuels upon the emissions of hydrocarbons is not as easily discerned as the effect upon carbon monoxide emissions. Part of the reason can be found in the fact that the constituents of "unburned fuel" in the case of methanol are different than those for gasoline. Considerable care must be taken in the hydrocarbon emission measurement procedure to account for all of these constituents that may be present.

When methanol blends are used as fuels, the possibility of increased emissions of formaldehyde in the exhaust exists. The use of methanol blends as a motor fuel has, in many cases, been shown to decrease the hydrocarbon emissions slightly as compared to the use of gasoline. This effect is caused by the leaner operation afforded by the use of methanol blends in the unmodified automobile. The beneficial effect is not as pronounced or reproducible as the decrease in carbon monoxide emissions when methanol blends are used. The levels of HC emissions were not lowered enough to meet the 1977 Federal Standards and the use of a catalytic converter will be necessary to meet these standards.

Oxides of Nitrogen Emissions (2,5,6,14,21,25,30)

The effect of the use of methanol blends upon the emission of oxides of nitrogen (NO_x) from a motor vehicle is pronounced, although not uniform from vehicle to vehicle. Nitrogen oxide emissions are maximized for the operation of a motor vehicle engine under conditions near stoichiometric combustion. Therefore, if the vehicle is originally adjusted to operate at or near an equivalence ratio of unity on gasoline and not modified when a methanol blend is substituted, the

leaning effect of the blend should reduce the NO $_{\rm x}$ emissions. If the vehicle originally operated fuel rich, however, this same leaning effect should increase the NO $_{\rm x}$ emissions.

When used in an unmodified vehicle, methanol blends have been shown to decrease nitrogen oxide emissions when the vehicle was of recent vintage, operating at or near stoichiometric conditions on gasoline. Tests on vehicles as old as 1970 showed such an effect; however, tests on a 1967 vehicle which originally operated fuel rich showed an increase in NO_{X} emissions. The blending of methanol into motor fuel has not reduced NO_{X} emissions below the 1977 Federal Standard, and the use of emission control devices will be necessary.

II. Pure Methanol as a Motor Vehicle Fuel

The use of either analytic or commercial grade methanol or methyl-fuel alone as a fuel for motor vehicles has also been suggested. As described in the preceding section, there are many problems associated with the use of blends of methanol and gasoline as a motor fuel, principally in the area of phase separation caused by the presence of water and the attendant alterations necessitated in the fuel distribution system. The separation problem is eliminated when pure methanol is used as a vehicle fuel; however, when this is done certain modifications to the vehicle itself become necessary. These modifications are considered to be more feasible particularly in the case where pure methanol is considered as the fuel for fleets of vehicles.

Economy (5,8,11,14,17,18,20,22,24,25,27,32,33,34,35,36,37)

Methanol possesses the lowest heating value of all the alcohols because it contains a higher percentage of oxygen by weight. Its heating value per gallon and per pound is approximately one-half that of gasoline. Theoretically, for the same performance, it should require twice as much methanol as gasoline per mile in the same vehicle. However, the high octane number, low volatility, high heat of vaporization and low heat of combustion of methanol can be put to good use in raising the thermal efficiency of engines. Because of the greater thermal efficiency afforded with the use of methanol, the number of miles travelled per BTU can be greater for methanol than for gasoline. As a result, the cost per mile can be lower for methanol fuel than for gasoline.

The use of methanol as a motor fuel has been shown to increase the thermal efficiency of internal combustion engines normally fuelled with gasoline. This increase is due to the possibility of using methanol at much leaner equivalence ratios and the possibility of utilizing higher compression ratios, as well as the elimination of certain emission controls that are deleterious to fuel economy. This increase in efficiency has been shown to be approximately 20 percent. Assuming that methanol is priced on an equal cost per BTU basis as gasoline, these savings will be reflected in the costs per mile to operate an equivalent vehicle.

Power (11,14,17,20,24,27,32,34,35,36,37,38)

For a stoichiometrically correct air to fuel ratio (6.45 for methanol,15.3 for gasoline) the energy densities of the fuels are very nearly equal (94.5 BTU/ft³for methanol,95.5 BTU/ft³for gasoline) indicating that equal power can be extracted from comparable engines using these fuels. Methanol will extract more brake-mean-effective pressure from an engine than will gasoline because of the increased volumetric efficiency afforded by the cooler methanol charge.

Equal power output has been achieved with methanol in an engine usually operated on gasoline when stoichiometric mixtures were used. Power

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output has been raised significantly above that for gasoline when richer mixtures were used; however, to gain the benefits in economy afforded by the lower lean misfire limit of methanol, this excess in power will have to be forfeited and possibly a slight loss in power sustained. For equivalent exhaust emissions, the methanol fueled engine has been shown to exhibit significantly higher power than the emission control equipped gasoline engine.

Driveability

Several of the driveability problems associated with the use of blends of methanol and gasoline are eliminated when pure methanol is used as a fuel; however, there remain problems associated with the vaporization properties of pure methanol as compared with those of gasoline.

Vapor Pressure (17,18,19,20,27,36,37)

Driveability (1,15,17,24,27,36)

The vaporization characteristics of pure methanol have caused some problems when it is used as a motor fuel. Its high heat of vaporization requires an enhanced supply of heat to the intake manifold in order to assure adequate mixture distribution to the cylinders. Its lower vapor pressure has made cold starting difficult and may necessitate the use of high volatility additives during this phase of the vehicle operation. Its low boiling point requires careful attention to keeping the fuel lines and carburetor shielded from excess heat. All of these problems have been encountered and several solutions developed.

The power output of a vehicle fueled with pure methanol can be equivalent to a comparable gasoline fueled vehicle, and the solubility and separability problems of blends do not exist for pure methanol fuels. Most of the subjective evaluations of the driveability of vehicles fueled with pure methanol have focused on the problems associated with cold starting of such vehicles.

The higher heat of vaporization of methanol together with the requirement of over twice as much methanol as gasoline for the same amount of air to form a stoichiometric mixture require that much more heat be supplied to the intake manifold to avoid cold starting and acceleration problems. Several solutions to these problems have been proposed. It is possible to add high vapor pressure liquids or gases such as butane either generally or preferably only during cold start situations. Either gasoline or LPG could be injected at cold at cold starts to accomplish the same effect. Aside from the cold start problem, the performance of the methanol fueled vehicle has been shown to be equivalent to a gasoline fueled vehicle.

Pure Fuel-Corrosion and Compatibility (1,6,14,17,26)

Several corrosion and compatibility problems associated with the use of methanol in blends with gasoline as a motor fuel have been described. There has been much less experience reported concerning the use of pure methanol as a motor fuel. Many of the problems encountered with the use of blends may also appear during pure fuel use, but this has not been proven by experience. Significant corrosion occurs after water causes separation of gasoline and methanol-water phases in blends. Much of this corrosion may be caused by the water in the lower phase. This separation does not take place when pure methanol is utilized as a motor fuel. Water is highly soluble in pure methanol and any traces found in the fuel system will be taken into the solution. The compatibility

problems associated with the use of pure methanol as a motor fuel have been more extensively investigated. It may be expected that compatibility problems between pure methanol and Viton fuel system elements, metacrylate fuel filters and possibly certain types of fuel pump diaphragms and gaskets may exist.

The limited experience with the use of pure methanol as a motor fuel has uncovered some compatibility problems with certain fuel system components. Some test vehicles have suffered no corrosion or compatibility problems, and others have required alterations to avoid them. There is a need for further fleet testing in which the problems of corrosion and materials compatibility with pure methanol motor fuel are more completely investigated. It will only be through the experience gained during such fleet tests that all of these problems can be uncovered.

Pure Fuel-Performance-Reliability and Conversions (1,5,8,12,13,14,15,17,20,27,31,36,37,39,40)

The reliability of motor vehicles that have been converted to operation on pure methanol fuel has proven to be as high as that of comparable gasoline fueled vehicles in several cases. The conversions necessary to enable a vehicle to operate with pure methanol as a fuel can be divided into two phases. Because the energy per cubic foot of stoichiometric mixtures of methanol and gasoline fuels is very similar, the modifications necessary to convert a conventional gasoline engine to pure methanol fuel are relatively simple. These conversions, to enable the use of pure methanol fuel in conventional engines will be called first phase conversions. Such conversions involve changes to the carburetor, intake manifold, fuel system, and spark advance curve and do not require major engine modifications. This phase of engine modification may be easily carried out on a fleet of automobiles and has been done in several cases. In addition, major engine modifications such as an increase in the compression ratio may be made in order to take advantage of the higher octane number of methanol in order to produce better thermal efficiency and an increase in fuel mileage. These modifications constitute a second phase of possible engine conversions. No full scale tests of such conversions have been reported.

Some modifications will be necessary to convert a conventional engine from gasoline to methanol fuel. Larger carburetor jets will be needed to provide the richer mixtures necessary, and larger fuel tanks will be needed to provide the same range of operation. It is also anticipated that some elastomeric seals in the fuel system may have to be changed depending upon their compatibility with methanol. Viton is the only material that has specifically caused problems in this area. Evaporative control cannisters and methacrylate fuel filters will have to be changed. Carburetor or fuel tank substitutions may be necessary on certain vehicles because of corrosion problems. possible corrosion and compatibility problems are not well defined and require an enlarged fleet test program to uncover them. Some means of assuring fuel vaporization and even distribution to the cylinders will have to be provided. This can be accomplished by placing heat exchangers in the intake manifold or by the adoption of a fuel injection system. Provisions will be necessary to assist in cold starting engines at ambient temperatures below 55 °F. This can be accomplished by the injection of butane, propane, acetone, ethyl ether, gasoline, or LPG during the starting procedure. The adoption of fuel injection would benefit in this area as well. Depending upon the particular vehicle and its fuel system layout there may be problems with vapor lock

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during hot operation. The installation of an electric fuel pump should eliminate these.

<u>Carbon Monoxide Emissions</u> (1,5,17,20,25,27,31,32, 35,36,40,41,42)

Since the methanol molecule has no carbon to carbon bonds and already contains one oxygen atom, the reaction kinetics for complete oxidation of this fuel are theoretically less complex than those for gasoline and the intermediate reaction products that form exhaust emissions are more readily eliminated from the exhaust system. In addition, it has been shown earlier that methanol fuelled vehicles will operate satisfactorily at much leaner mixture ratios. Therefore, it may be expected that vehicles fueled by pure methanol, especially those equipped with catalytic muffler will emit less carbon monoxide than comparable gasoline fuelled vehicles. This reduction has been measured except in those cases in which operation was fuel-rich. The extended fuel-rich warm-up period necessary with methanol fuelled vehicles appreciably raises their CO emissions. The installation of a catalytic converter has been shown to reduce CO emissions below the 1977 Federal Standard.

<u>Hydrocarbon Emissions</u> (1,5,14,15,17,18,20,27,32, 34,35,36,38,40,41)

Several tests have been performed on methanol fuelled vehicles from which the emissions of hydrocarbons and unburned fuel have been reported. Some hydrocarbons emitted in the exhaust of methanol fuelled vehicles are different than those emitted by gasoline fuelled vehicles and adequate provisions must be made to insure that the recording equipment accurately measures their presence. The major component of unburned fuel in the exhaust has been found to be methanol which is technically not a hydrocarbon at all; however, the emissions of unburned fuel are generally reported under the heading of hydrocarbon emissions.

The leaner operation afforded by the use of methanol fuel should lead to lower hydrocarbon (HC) emissions. The emissions of hydrocarbons and unburned fuel from engines fuelled by methanol have been shown to be lower than those fuelled by gasoline during hot start emissions tests. Because of the longer warm-up period under fuel rich operation which is necessary with methanol fuel, the HC emissions from methanol fuel were higher than those from gasoline during cold start tests. The use of a catalytic muffler was found to be necessary in order to meet the 1977 Federal HC Standard. There are no aromatics emitted among the hydrocarbons in the exhaust of a methanol fuelled vehicle, and there is correspondingly less carcenogenic risk from these emissions. It is also expected that the total reactivity caused by the unburned fuel for the formation of photochemical air pollution is much lower for a methanol fuelled vehicle than for gasoline.

Oxides of Nitrogen Emissions (1,5,14,15,17,18,20,27,32,33, 34,35,36,37,38,40,41,42)

The emissions of oxides of nitrogen $(\mathrm{NO_X})$ in the exhausts of methanol fuelled vehicles have been demonstrated to be very low; lower than the $\mathrm{NO_X}$ emissions of comparable gasoline fuelled vehicles. Emission levels below the 1977 Federal $\mathrm{NO_X}$ standard have been demonstrated with methanol fuelled vehicles without the use of emission control equipment. Results have shown no increase in $\mathrm{NO_X}$ emissions during cold start tests. Calculations have shown that the peak Otto cycle temperature of methanol fuel is lower than that of iso-octane. The lower combustion temperature of methanol contributes to the depression of $\mathrm{NO_X}$ emissions from methanol fueled vehicles. The higher flame velocity

exhibited by methanol as compared to that of gasoline allows the use of later spark timing which also results in lower $\text{NO}_{\mathbf{X}}$ emissions. Since emissions of $\text{NO}_{\mathbf{X}}$ peak at stoichiometric conditions of operation, the lower lean misfire limit exhibited by methanol permits lower $\text{NO}_{\mathbf{X}}$ emissions by allowing operation at much leaner mixture ratios than gasoline.

Aldehyde Emissions (1,18,27,32,35,36,38,41)

Aldehydes form a class of potential air pollutants that are not presently covered by Federal Standards. The presence of certain aldehydes, principally formaldehyde and acetaldehyde has been measured in the exhaust of methanol fuelled engines. Aldehyde emissions from automobiles have not been measured as extensively as those of other air pollutants. There exists no Federal Standard for aldehyde emissions. The level of aldehyde emissions from methanol fuelled vehicles seems to be a sensitive function of the air to fuel mixture ratios. Some tests have shown that the aldehyde emission level from methanol fuelled vehicles is no higher than the level from comparable gasoline fuelled vehicles. Others have shown increased aldehyde emissions when methanol is substituted for gasoline as a fuel. There is a need for further testing of both methanol fuelled vehicles and gasoline fuelled vehicles, however, before any definite conclusions can be drawn. The use of a catalytic muffler has been shown to considerably reduce the aldehyde emissions of methanol fuelled automobiles.

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